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<p>(21) International Application Number: PCT/US97/17458</p> <p>(22) International Filing Date: 29 September 1997 (29.09.97)</p> <p>(71) Applicant (for all designated States except US): MINNESOTA MINING AND MANUFACTURING COMPANY [US/US]; 3M Center, P.O. Box 33427, Saint Paul, MN 55133-3427 (US).</p> <p>(72) Inventors; and</p> <p>(75) Inventors/Applicants (for US only): DAMS, Rudolf, J. [BE/BE]; Schuttershof 19, B-2070 Zwijndrecht (BE). QIU, Zai-Ming [CN/US]; 3089 Copper Oaks Court, Woodbury, MN 55125 (US). SMOLDERS, Robert, Remi, Louis [BE/BE]; Runcvoort 15, B-2170 Merksem (BE). COPPENS, Dirk, M. [BE/BE]; Tijmstraat 30, B-9120 Melsek (BE). NAGASE, Makoto [JP/JP]; 501, 2-214-6 Manami-Ohsawa, Hachioji-City, Tokyo 192-03 (JP).</p> <p>(74) Agents: MAKI, Eloise, J. et al.; Minnesota Mining and Manufacturing Company, Office of Intellectual Property Counsel, P.O. Box 33427, Saint Paul, MN 55133-3427 (US).</p>		<p>(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).</p> <p>Published With international search report.</p>
<p>(54) Title: SPECIFIC FLUORINATED ETHERS AS REACTION MEDIUM</p> <p>(57) Abstract</p> <p>The invention provides a method for preparing a desired organic compound by reacting one or more reactants in a reaction medium comprising a fluorinated ether compound wherein the fluorinated ether compound comprises at least 3 carbon atoms and a perfluorinated moiety that is linked through ether oxygen atoms to one or more hydrocarbon moieties. The invention also provides certain products as a result of carrying out the aforementioned methods and methods of using such compositions to treat substrates like fabrics or electronic components.</p>		

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SPECIFIC FLUORINATED ETHERS AS REACTION MEDIUM

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Field of the Invention

The present invention relates to the preparation of organic compounds in a fluorinated ether as reaction medium.

10 Background of the Invention

Organic reactions for the preparation of organic compounds are in many instances carried out in a reaction medium which is often in liquid form under the reaction conditions. The reaction medium often acts as a solvent for one or more of the reactants that are involved in the preparation of a desired organic compound.

15 Many different organic reactions are known and they include reactions such as polymerization, including free radical polymerization, polycondensation, additions, substitutions, reduction and oxidation. It is well recognized that the reaction medium plays an important role in the preparation of an organic compound and in particular may have an influence on the yield of the organic product. Many
20 different reaction media have heretofore been proposed and used for the preparation of various organic compounds. Such reaction media include both "hydrocarbon" type media which are substantially free of fluorine as well as certain fluorinated reaction media.

The latter have particularly been used in situations where one of the
25 reactants is a fluorinated compound that needs to be dissolved in the reaction medium. Certain fluorinated reaction media have also been used where inertness of the reaction medium is required and/or when non-flammability is an important issue. For example, U.S. Patent No. 5,182,342 discloses the use of certain hydrofluorocarbon solvents for the polymerization of certain fluoromonomers
30 containing a vinylic fluorine atom. The disclosed hydrofluorocarbon solvents are saturated and:

optionally, contain one carbon-carbon double bond;

contain carbon, fluorine, at least one hydrogen atom bound to a carbon atom, and optionally one or more ether oxygen atoms or one or more alcohols or one or more ether oxygen atoms and one or more alcohols;

- 5 contain at least as many fluorine atoms as hydrogen atoms;
optionally, contain one or more $-\text{CF}_2\text{OCH}_3$ group(s);
contain no more than two adjacent $-\text{CH}_2-$ groups; and
have no hydrogen atoms on any primary carbon.

Other solvents described for use in the polymerization of various
10 fluoromonomers are compounds containing (besides carbon): chlorine, fluorine and
hydrogen (see for example U.S. Patent Nos. 4,499,249, 4,714,756, 3,635,926,
4,029,868, 3,528,954, and Re. 32,199); fluorine (see for example U.S. Patent
Nos. 3,635,926, Re.32,199, 4,499,249, and 4,948,844); and chlorine and fluorine
(see U.S. Patent No. 4,948,844).

- 15 U.S. Patent. No. 3,616,371 discloses the use of various fluorinated solvents
for use in the polymerizations to form homo- or copolymers of vinylidene fluoride.
U.S. Patent. No. 4,123,602 discloses the use of various fluorocarbon type solvents.
Perfluorocarbons, have also been proposed as solvents for these polymerizations.

Many of the fluorinated solvents proposed so far for the polymerization of
20 fluoromonomers have a fairly low solubility for many organic compounds including
fluorine-free comonomers. Moreover, the chlorofluorocarbons (CFCs) have been
linked to ozone depletion while the perfluorocarbons contribute to the green house
effect.

- WO 93/24586 discloses compositions that include at least one fluoroether
25 and at least one hydrofluorocarbon. Included in the disclosure are compositions of
a cyclic or acyclic hydrofluoroether of the formula $\text{C}_a\text{F}_b\text{H}_{2a+2-b}\text{O}_c$ wherein $a=2$ or 3
and $3 \leq b \leq 8$ and $c=1$ or 2 and a hydrofluorocarbon of the formula $\text{C}_n\text{F}_m\text{H}_{2n+2-m}$
wherein $1 \leq n \leq 4$ and $1 \leq m \leq 8$. The compositions are alleged to be useful for a variety
of applications including the use as polymerization medium. Amongst the
30 exemplified hydrofluoroethers there is mentioned trifluoromethyl methyl ether
which has a boiling point of -24.2°C .

Summary of the Invention

The present invention provides a method for preparing a desired organic compound by reacting one or more reactants in a reaction medium, said reaction
5 medium comprising a fluorinated ether compound comprising at least 3 carbon atoms and a perfluorinated moiety that is linked through ether oxygen atoms to one or more hydrocarbon moieties.

The term "desired organic compound" means an organic compound that is purposely prepared for an envisaged application or as an intermediate in the
10 preparation of another organic compound. The organic compound can be a simple organic compound which may be polymerizable or not, a polymeric compound or an oligomeric compound.

The term "ether compound" includes compounds containing one or more ether oxygen atoms.

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Detailed Description of the Invention

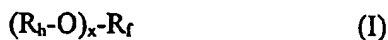
In accordance with the present invention, it was found that certain fluorinated ethers are useful as reaction medium in a variety of reactions for preparing an organic compound. In particular, the fluorinated ethers employed in
20 the invention have good solvency power and can be used to dissolve many different organic reactants. Moreover, the desired solvency of the fluorinated ether can be tailored by appropriate selection of the perfluorinated moiety and hydrocarbon moiety making it possible to select a fluorinated ether that is a better solvent for the reactants than for the desired organic compound. This allows the desired organic
25 product to be readily separated from the reaction medium which is particularly advantageous where the desired organic product is a polymer. Furthermore, the fluorinated ethers employed in the invention are highly inert solvents. The fluorinated ethers can also be selected to have low or no flammability under the reaction conditions employed. As taught in GB 2274462, hydrofluorocarbons, perfluorocarbons and fluorinated alkyl ethers are generally non-flammable if the
30 number of C-F bonds exceeds the sum of the number of C-H and C-C bonds.

However for safety considerations, the flammability and flash points of such compounds should be experimentally determined.

The fluorinated ethers employed in the invention are also much less toxic than many organic solvents used as reaction media, are available in a wide variety of boiling points and are liquids over a wide temperature range at atmospheric pressure. For example, 1-methoxynonafluorobutane has a freezing point of -135°C and a boiling point of 60°C thus providing a liquid working range of 195°C with very little change in viscosity. The fluorinated ethers also have a low water solubility (typically less than 10 ppm) making them especially suitable in reactions that are sensitive to water. Finally, the fluorinated ethers have a vapor considerably denser than air and they can therefore be used to create a gaseous reaction environment free of oxygen and other ambient unwanted gasses.

Preferably, the fluorinated ethers comprise a perfluoroaliphatic moiety linked to one or more alkyl moieties through ether oxygen atoms. The perfluoroaliphatic moiety may contain one or more catenary heteroatoms such as oxygen, nitrogen or sulfur, although oxygen and nitrogen are preferred if present. More preferably, the perfluoroaliphatic moiety comprises two to ten carbon atoms and may optionally contain either oxygen and/or nitrogen catenary heteroatoms, and the alkyl moieties comprise one to four carbon atoms.

Particularly preferred fluorinated ethers correspond to the following formula:



wherein:

x is 1 or 2;

R_h represents an alkyl group having 1 to 4 carbon atoms;

R_f represents a perfluorinated aliphatic group comprising at least two carbon atoms, preferably between 2 and 9 carbon atoms, and optional catenary heteroatoms such as oxygen, nitrogen and sulfur atoms.

When x is 1, R_f preferably is selected from the group consisting of linear or branched perfluoroalkyl groups, perfluorocycloalkyl groups containing a perfluoroalkyl group, perfluorocycloalkyl groups, linear or branched perfluoroalkyl

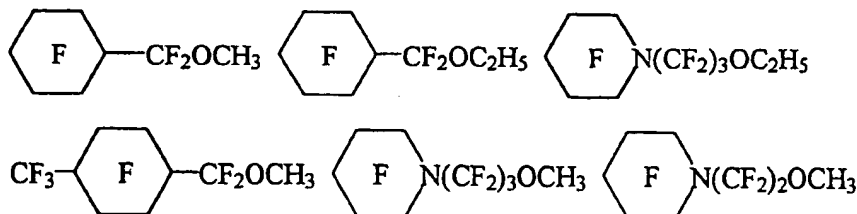
groups having one or more catenary heteroatoms, perfluorocycloalkyl groups containing a perfluoroalkyl group having one or more catenary heteroatoms and perfluorocycloalkyl groups having one or more catenary heteroatoms. Particularly preferred catenary heteroatoms include oxygen or nitrogen atoms.

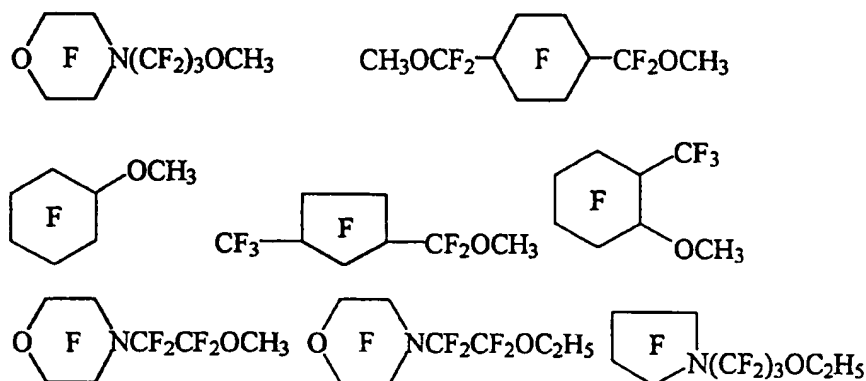
- 5 When x is 2, R_f is preferably selected from the group consisting of linear or branched perfluoroalkylene groups, perfluorocycloalkyl groups containing a perfluoroalkylene group, perfluorocycloalkylene groups, linear or branched perfluoroalkylene groups having one or more catenary heteroatoms, perfluorocycloalkyl groups containing a perfluoroalkylene group having one or
 10 more catenary heteroatoms and perfluorocycloalkylene groups having one or more catenary heteroatoms. Particularly preferred heteroatoms include oxygen and nitrogen atoms.

- More preferably, x is 1, and the compound is normally liquid or gaseous (i.e., liquid or gaseous under ambient conditions of temperature and pressure), R_f is
 15 selected from the group consisting of linear or branched perfluoroalkyl groups having from 3 to about 9 carbon atoms, perfluorocycloalkyl-containing perfluoroalkyl groups having from 5 to about 7 carbon atoms, and perfluorocycloalkyl groups having from 5 to about 6 carbon atoms; R_h is a methyl or ethyl group; R_f can contain one or more catenary heteroatoms; and the sum of
 20 the number of carbon atoms in R_f and the number of carbon atoms in R_h is greater than or equal to 4.

Representative examples of fluorinated ethers suitable for use in the processes and composition of the invention include the following compounds:

- $n\text{-C}_4\text{F}_9\text{OCH}_3$, $n\text{-C}_4\text{F}_9\text{OCH}_2\text{CH}_3$, $\text{CF}_3\text{CF}(\text{CF}_3)\text{CF}_2\text{OCH}_3$, $\text{CF}_3\text{CF}(\text{CF}_3)\text{CF}_2\text{OC}_2\text{H}_5$,
 25 $\text{C}_8\text{F}_{17}\text{OCH}_3$, $\text{CH}_3\text{O}-(\text{CF}_2)_4-\text{OCH}_3$, $\text{C}_5\text{F}_{11}\text{OC}_2\text{H}_5$, $\text{C}_3\text{F}_7\text{OCH}_3$, $\text{CF}_3\text{OC}_2\text{F}_4\text{OC}_2\text{H}_5$,
 $\text{C}_3\text{F}_7\text{OCF}(\text{CF}_3)\text{CF}_2\text{OCH}_3$, $(\text{CF}_3)_2\text{CFOCH}_3$, $(\text{CF}_3)\text{COCH}_3$, $\text{C}_4\text{F}_9\text{OC}_2\text{F}_4\text{OC}_2\text{F}_4\text{OC}_2\text{H}_5$,
 $\text{C}_4\text{F}_9\text{O}(\text{CF}_2)_3\text{OCH}_3$,





and 1,1-dimethoxyperfluorocyclohexane.

5 The fluorinated ethers suitable for use in the process of the invention can be prepared by alkylation of perfluorinated alkoxides prepared by the reaction of the corresponding perfluorinated acyl fluoride or perfluorinated ketone with an anhydrous alkali metal fluoride (e.g., potassium fluoride or cesium fluoride) or anhydrous silver fluoride in an anhydrous polar, aprotic solvent. (See, e.g., the preparative methods described in French Patent Publication No. 2,287,432 and German Patent Publication No. 1,294,949.) Alternatively, a fluorinated tertiary alcohol can be allowed to react with a base, e.g., potassium hydroxide or sodium hydride, to produce a perfluorinated tertiary alkoxide which can then be alkylated by reaction with alkylating agent.

15 Suitable alkylating agents for use in the preparation include dialkyl sulfates
(e.g., dimethyl sulfate), alkyl halides (e.g., methyl iodide), alkyl p-toluenesulfonates
(e.g., methyl p-toluenesulfonate), alkyl perfluoroalkanesulfonates (e.g., methyl
perfluoromethanesulfonate), and the like. Suitable polar, aprotic solvents include
acyclic ethers such as diethyl ether, ethylene glycol dimethyl ether, and diethylene
20 glycol dimethyl ether; carboxylic acid esters such as methyl formate, ethyl formate,
methyl acetate, diethyl carbonate, propylene carbonate, and ethylene carbonate;
alkyl nitriles such as acetonitrile; alkyl amides such as N,N-dimethylformamide,
N,N-diethylformamide, and N-methylpyrrolidone; alkyl sulfoxides such as dimethyl
sulfoxide; alkyl sulfones such as dimethylsulfone, tetramethylene sulfone, and other
25 sulfolanes; oxazolidones such as N-methyl-2-oxazolidone; and mixtures thereof.

Perfluorinated acyl fluorides (for use in preparing the fluorinated ethers) can be prepared by electrochemical fluorination (ECF) of the corresponding

hydrocarbon carboxylic acid (or a derivative thereof), using either anhydrous hydrogen fluoride (Simons ECF) or $\text{KF} \cdot 2\text{HF}$ (Philips ECF) as the electrolyte. Perfluorinated acyl fluorides and perfluorinated ketones can also be prepared by dissociation of perfluorinated carboxylic acid esters (which can be prepared from the corresponding hydrocarbon or partially-fluorinated carboxylic acid esters by direct fluorination with fluorine gas). Dissociation can be achieved by contacting the perfluorinated ester with a source of fluoride ion under reacting conditions (see the method described in U.S. Patent No. 3,900,372 (Childs)) or by combining the ester with at least one initiating reagent selected from the group consisting of gaseous, non-hydroxylic nucleophiles; liquid, non-hydroxylic nucleophiles; and mixtures of at least one non-hydroxylic nucleophile (gaseous, liquid, or solid) and at least one solvent which is inert to acylating agents.

Initiating reagents which can be employed in the dissociation are those gaseous or liquid, non-hydroxylic nucleophiles and mixtures of gaseous, liquid, or solid, non-hydroxylic nucleophile(s) and solvent (hereinafter termed "solvent mixtures") which are capable of nucleophilic reaction with perfluorinated esters. The presence of small amounts of hydroxylic nucleophiles can be tolerated. Suitable gaseous or liquid, non-hydroxylic nucleophiles include dialkylamines, trialkylamines, carboxamides, alkyl sulfoxides, amine oxides, oxazolidones, pyridines, and the like, and mixtures thereof. Suitable non-hydroxylic nucleophiles for use in solvent mixtures include such gaseous or liquid, non-hydroxylic nucleophiles, as well as solid, non-hydroxylic nucleophiles, e.g., fluoride, cyanide, cyanate, iodide, chloride, bromide, acetate, mercaptide, alkoxide, thiocyanate, azide, trimethylsilyl difluoride, bisulfite, and bifluoride anions, which can be utilized in the form of alkali metal, ammonium, alkyl-substituted ammonium (mono-, di-, tri-, or tetra-substituted), or quaternary phosphonium salts, and mixtures thereof. Such salts are in general commercially available but, if desired, can be prepared by known methods, e.g., those described by M. C. Sneed and R. C. Brasted in *Comprehensive Inorganic Chemistry*, Volume Six (The Alkali Metals), pages 61-64, D. Van Nostrand Company, Inc., New York (1957), and by H. Kobler et al. in *Justus*

Liebigs Ann. Chem. 1978, 1937. 1,4-diazabicyclo[2.2.2]octane and the like are also suitable solid nucleophiles.

The reaction medium used in the preparation method of the present invention comprises the fluorinated ether optionally in combination with additional
5 compounds. Thus in accordance with the present invention, the reaction medium is comprised of those compounds that are substantially inert and do not substantially participate in the reaction to prepare the organic compound. It is further preferred that the reaction medium is non-flammable. Compounds that actively participate in an organic reaction include for example the reactants, a catalyst, scavengers,
10 precipitation aids, initiators, chain terminators and chain transfer agents. Suitable additional compounds for use together with the fluorinated ether as reaction medium are co-solvents that can increase the solvability of one or more of the reactants. Such co-solvents can be hydrocarbon solvents such as ketones, esters, alcohols and ethers. The amount of such a hydrocarbon co-solvent may vary widely
15 but it is preferred to use hydrocarbon co-solvent in an amount such that the reaction medium is non-flammable. Particularly suitable co-solvents for use with the fluorinated ether are those that are able to form an azeotropic mixture with the particular fluorinated ether. It is furthermore possible to use a mixture of two or more fluorinated ethers as the reaction medium. Preferably the reaction medium
20 comprises at least 50% by weight and more preferably at least 90 % by weight of the fluorinated ether.

The fluorinated ethers of the present invention can be used in a variety of organic reactions. Such organic reactions include free radical polymerizations, polycondensations, oxidation and reduction reactions, radical addition reactions,
25 nucleophilic addition reactions, electrophilic addition reactions and nucleophilic and electrophilic substitution reactions. The organic reactions can be of the type that require a catalyst. Such catalyst can be of acidic or basic nature or they may operate on an oxido-reduction mechanism. The fluorinated ethers are most suitable for use with acidic or weak basic catalysts or for use with catalysts that operate on
30 an oxido-reduction mechanism.

The fluorinated ethers are particularly suitable for use in organic reactions that involve one or more reactants that are fluorochemical compounds since the fluorinated ethers have good solvent properties for fluorochemical compounds. The fluorinated ethers however are also good solvents for many non-fluorinated
5 compounds which makes them especially suitable for use as reaction medium in reactions that involve both a fluorochemical and a non-fluorochemical reactant.

In accordance with one embodiment of the present invention, the fluorinated ethers can be used as a reaction medium, in particular as a liquid solvent, in the polymerization of a fluorochemical monomer. Typically the polymerization is a free
10 radical polymerization.

A fluorochemical monomer that can be polymerized in the reaction medium of the invention typically comprises a fluorinated group and an ethylenically unsaturated group free of fluorine. Preferably the fluorochemical monomer corresponds to the formula:



wherein

M_f represents a partially fluorinated or perfluorinated aliphatic group,

L^1 represents an organic divalent linking group, and

E represents an ethylenically unsaturated group.

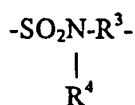
20 The ethylenically unsaturated group of preferred fluorochemical monomers is free of fluorine atoms.

A fluorochemical monomer according to formula (II) can be homopolymerised or copolymerized with other fluorochemical monomers of formula (II) and/or hydrocarbon monomers. In connection with the present
25 invention, the term "hydrocarbon monomer" means any substantially fluorine free monomer that contains hydrogen and carbon and optionally one or more non-interfering substituents. Preferably, such hydrocarbon monomer corresponds to the formula M_h-E' wherein M_h represents a fluorine free moiety and E' represents an ethylenically unsaturated group also free of fluorine atoms.

30 The fluoroaliphatic radical, M_f , in the fluorochemical monomer, is a fluorinated, stable, inert, preferably saturated, non-polar, monovalent aliphatic

radical. It can be straight chain, branched chain, or cyclic or combinations thereof. It can contain heteroatoms such as oxygen, divalent or hexavalent sulfur, or nitrogen. M_f is preferably a fully-fluorinated radical, but hydrogen or chlorine atoms can be present as substituents if not more than one atom of either is present for every two carbon atoms. The M_f radical has at least 3 and typically up to 18 carbon atoms, preferably 3 to 14, especially 6 to 12 carbon atoms, and preferably contains about 40% to about 80% fluorine by weight, more preferably about 50% to about 78% fluorine by weight. The terminal portion of the M_f radical is a perfluorinated moiety, which will preferably contain at least 7 fluorine atoms. e.g., $CF_3CF_2CF_2-$, $(CF_3)_2CF-$, F_3SCF_2- . Especially suitable monomers that can be polymerized in the present reaction medium are those of which the M_f radicals are fully or substantially fluorinated and are preferably those perfluorinated aliphatic radicals of the formula $C_nF_{2n+1}-$ where n is 3 to 18.

The linking group L^1 links the fluoroaliphatic group M_f to the free radical polymerizable group E. Linking group L^1 preferably contains from 1 to about 20 carbon atoms. L^1 can optionally contain oxygen, nitrogen, or sulfur-containing groups or a combination thereof, and L^1 is preferably free of functional groups that substantially interfere with free-radical polymerization (e.g., polymerizable olefinic double bonds, thiols, and other such functionality known to those skilled in the art). Examples of suitable linking groups L^1 include straight chain, branched chain or cyclic alkylene, arylene, aralkylene, oxy, oxo, hydroxy, thio, sulfonyl, sulfoxy, amino, imino, sulfonamido, carboxyamido, carbonyloxy, urethanylene, ureylene, and combinations thereof such as sulfonamidoalkylene. Typical linking groups are selected from the group consisting of alkylenes, poly(oxyalkylenes) having 1 to 4 oxyalkylene groups and organic divalent linking groups according to the following formula:



wherein

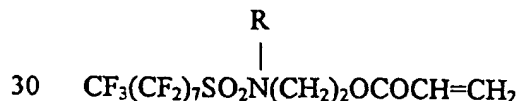
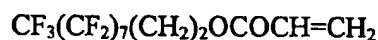
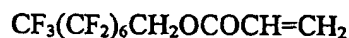
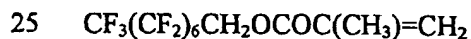
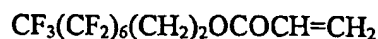
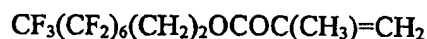
R^3 represents a linear or branched alkylene having 2, 3 or 4 carbon atoms,
and

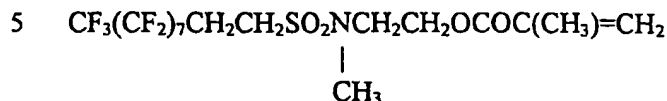
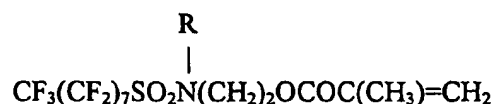
R⁴ represents an alkyl having 1 to 4 carbon atoms.

E and E' are free radically polymerizable groups that typically contain an ethylenically unsaturated group capable of polymerization with itself or each other. A particularly preferred ethylenically unsaturated group is an α,β ethylenically unsaturated carbonyl group such as in an acrylate or methacrylate. Suitable groups include, for example, moieties derived from vinyl ethers, vinyl esters, allyl esters, vinyl ketones, styrene, vinyl amide, acrylamides, maleates, fumarates, acrylates and methacrylates. Of these, the esters of alpha, beta unsaturated acids, such as the acrylates and methacrylates are preferred.

Fluorochemical monomers M_r-L¹-E as described above and methods for the preparation thereof are known and disclosed, e.g., in U.S. Patent No. 2,803,615, which description is incorporated herein by reference. Examples of such compounds include general classes of fluorochemical acrylates, methacrylates, vinyl ethers, and allyl compounds containing fluorinated sulfonamido groups, acrylates or methacrylates derived from fluorochemical telomer alcohols, acrylates or methacrylates derived from fluorochemical carboxylic acids, and perfluoroalkyl acrylates or methacrylates as disclosed in EP-A-526 976, which description is incorporated herein by reference.

Specific examples of fluorochemical monomers include :





Where: R=methyl, ethyl or n-butyl.

- 10 Suitable hydrocarbon monomers are also well known and generally commercially available. Examples of such compounds include general classes of ethylenic compounds capable of free-radical polymerization, such as, for example, allyl esters such as allyl acetate and allyl heptanoate; alkyl vinyl ethers or alkyl allyl ethers such as cetyl vinyl ether, dodecylvinyl ether, 2-chloroethylvinyl ether,
- 15 ethylvinyl ether; unsaturated acids such as acrylic acid, methacrylic acid, alpha-chloro acrylic acid, crotonic acid, maleic acid, fumaric acid, itaconic acid and their anhydrides and their esters such as vinyl, allyl, methyl, butyl, isobutyl, octadecyl, hexyl, heptyl, 2-ethyl-hexyl, cyclohexyl, lauryl, stearyl, isobornyl or alkoxy ethyl acrylates and methacrylates; 2-hydroxyethyl methacrylate ester of acetoacetic acid,
- 20 dicyclopentenylloxy ethyl methacrylate, (3-chloro-2-hydroxypropyl)-methacrylate, alpha-beta unsaturated nitriles such as acrylonitrile, methacrylonitrile, 2-chloroacrylonitrile, 2-cyanoethyl acrylate, alkyl cyanoacrylates; alpha, beta-unsaturated carboxylic acid derivatives such as allyl alcohol, allyl glycolate, acrylamide, methacrylamide, diisopropyl acrylamide, dimethyl acrylamide,
- 25 diacetoacrylamide, N,N-diethylaminoethylmethacrylate, N-t-butylamino ethyl methacrylate; styrene and its derivatives such as vinyltoluene, alpha-methylstyrene, alpha-cyanomethyl styrene; lower olefinic hydrocarbons which can contain halogen such as ethylene, propylene, isobutene, 3-chloro-1-isobutene, isoprene, and allyl or vinyl halides such as vinyl and vinylidene chloride. Preferred co-monomers which
- 30 can be copolymerized with the above-described fluorinated monomers include those selected from octadecylmethacrylate, laurylmethacrylate, butylacrylate, N-methylol acrylamide, isobutylmethacrylate, ethylhexyl acrylate, ethylhexyl methacrylate, glycidyl methacrylate, vinylchloride and vinylidene chloride.

Free radical polymerization of the above fluorochemical monomers optionally in combination with one or more hydrocarbon monomers can be thermally or photochemically initiated. Preferably, the polymerization is initiated by a free radical initiator. Typical examples thereof include azo compounds such as

5 azobisisobutyronitrile, 2,2'-azobis[N-(4-chlorophenyl)-2-methylpropionamidine]-dihydrochloride; 2,2'-azobis[N-(4-hydroxyphenyl)-2-methylpropionamidine]dihydrochloride; 2,2'-azobis[N-(4-aminophenyl)-2-methylpropionamidine]tetrahydrochloride; 2,2'-azobis[2-methyl-N-2-propenylpropionamidine]dihydrochloride; 2,2'-azobis[N-(2-hydroxyethyl)-2-

10 methylpropionamidine]dihydrochloride; 2,2'-azobis[2-methyl-N-(2-hydroxyethyl)propionamide]; 2,2'-azobis[2-(hydroxymethyl)propionitrile]; 2,2'-azobis(2,3-dimethyl valeronitrile) 2,2'-azobis{2-methyl-N-[1,1-bis(hydroxymethyl)-2-hydroxyethyl]propionamide}; and 2,2'-azobis{2-methyl-N-[1,1-

15 bis(hydroxymethyl)ethyl]propionamide} and hydroperoxides such as cumene, t-butyl, and t-amyl hydroperoxide, dialkyl peroxides such as di-t-butyl and dicumylperoxide, peroxyesters such as t-butylperbenzoate and di-t-butylperoxy phthalate, diacylperoxides such as benzoyl peroxide and lauroyl peroxide.

It was found that the polymerization in the fluorinated ether as reaction medium, typically can yield high molecular weight polymers. Furthermore, due to

20 the good solvent properties of the fluorinated ether for both hydrocarbon and fluorochemical monomer, copolymers can be prepared that are otherwise difficult to prepare. In particular, the fluorinated ethers are excellent solvents for the copolymerization of fluorochemical (meth)acrylates with hydrocarbon (meth)acrylates and especially for copolymerization with (meth)acrylic acid.

25 The resulting fluorochemical compositions comprising (a) a copolymer of a fluorochemical monomer comprising a fluorinated group and an ethylenically unsaturated group free of fluorine and a non-fluorinated monomer and (b) the fluorinated ether are particularly suitable for use as protective coatings. Accordingly the fluorochemical composition can be applied to a substrate such as

30 for example copper, aluminum, steel, tin and glass. According to a particular embodiment of this invention, the fluorochemical composition is applied to an

electronic component. Typical application methods include dipping, brushing or spraying. Dipping is typically preferred as it yields a uniform film. The resulting film is chemically inert and provides good repellency properties, in particular the resulting film is readily repellent to water, oils (including silicone oils) and solvents including heptane and toluene.

The fluorochemical composition typically comprises an amount of 0.01% by weight to 50% by weight of the copolymer. Further, the copolymer may be dissolved or dispersed in the fluorinated ether. Preferably, the fluorochemical composition comprises between 1 and 10% by weight of the copolymer. The fluorinated ether used in the fluorochemical composition for use as a protective coating may further be blended with a perfluorinated hydrocarbon or trans-dichloroethylene.

The polymerization may further be carried out in the presence of an end-capping agent or chain transfer agent to tailor the molecular weight of a polymer prepared or to prepare an oligomer which comprises only a few monomer units, typically from 2 to 50 monomer units. Such compound can be functionalized for further reaction which is particularly desirable in case an oligomer is prepared.

Suitable functional groups for inclusion in the end-capping agent include hydroxy, amino, halo, epoxy, haloformyl, aziridiny, acid groups and salts thereof, quaternary ammonium groups and salts thereof. Examples of such chain transfer agents include:

2-mercaptoethanol, mercaptoacetic acid, 2-mercaptobenzimidazole,
2-mercaptobenzoic acid, 2-mercaptobenzothiazole, 2-mercaptobenzoxazole,
3-mercapto-2-butanol, 2-mercaptosulfonic acid, 2-mercaptoethyl ether,
2-mercaptoethylsulfide, 2-mercaptoimidazole, 8-mercaptomenthone,
2-mercaptonicotinic acid, 4-hydroxythiophenol, 3-mercapto-1,2-propanediol,
1-mercapto-2-propanol, 2-mercaptopropionic acid,
N-(2-mercaptopropionyl)glycine, 3-mercaptopropyltrimethoxysilane,
2-mercaptopyridine, 2-mercaptopyridine-N-oxide, 2-mercaptopyridinol,
2-mercaptopyrimidine, mercaptosuccinic acid, 2,3-dimercaptopropanesulfonic
acid, 2,3-dimercaptopropanol, 2,3-dimercaptosuccinic acid,

2,5-dimercapto-1,3,4-thiadiazole, 3,4-toluenedithiol, o-, m-, and p-thiocresol, 2-mercaptoethylamine, ethylcyclohexanedithiol, p-menthane-2,9-dithiol, 1,2-ethanedithiol, cysteine, cystein hydrochloride, cysteine ethylester. Preferred functionalized end-capping agents include

5 2-mercaptoethanol, 3-mercapto-1,2-propanediol, 4-mercaptopropanol, 11-mercaptoundecanol, mercaptoacetic acid, 3-mercaptopropionic acid, 12-mercaptododecanoic acid, 2-mercaptoethylamine, 1-chloro-6-mercapto-4-oxahexan-2-ol, 2,3-dimercaptosuccinic acid, 2,3-dimercaptopropanol, 3-mercaptopropyltrimethoxysilane,

10 2-chloroethanethiol, 2-amino-3-mercaptopropionic acid, and compounds such as the adduct of 2-mercaptoethylamine and caprolactam.

Non-functionalized end-capping agents or chain transfer agents are those that contain a group capable of terminating a radical chain reaction (e.g., a thiol) but no further functional groups. Such compounds include mono, di, and polythiols

15 such as ethanethiol, propanethiol, butanethiol, hexanethiol, n-octylthiol, t-dodecylthiol, 2-mercaptoethyl ether, 2-mercaptoimidazole, and the like.

The fluorinated ethers of the present invention are also excellent reaction media for the homo- or copolymerization of hydrocarbon monomers not involving a fluorochemical monomer. Suitable hydrocarbon monomers that can be homo- or

20 copolymerized in a reaction medium comprising the fluorinated compound are those listed above. The fluorinated ethers used in the present invention allow for the preparation of very high molecular weight polymers of hydrocarbon monomers and due to their excellent solvent properties for these monomers, copolymers can be prepared of hydrocarbon monomers which in other solvents might otherwise be

25 difficult or impossible to prepare. For example, the fluorinated ethers of the present invention are particularly suitable to prepare copolymers of alkyl acrylates wherein the alkyl group contains at least 4 carbon atoms and/or alkyl methacrylates wherein the alkyl group contains at least 4 carbon atoms and acrylic or methacrylic acid. It was found that such polymers could be readily prepared in the fluorinated ether and

30 could be easily separated therefrom after polymerization. This stands in contrast to other common solvents such as ethylacetate used for this polymerization that may

yield nonhomogenous polymers, in particular when methacrylic acid is the comonomer.

Examples of long chain alkyl(meth)acrylates that can be copolymerized with acrylic or methacrylic acid include n-butyl, n-pentyl, n-hexyl, cyclohexyl, isoheptyl, n-nonyl, n-decyl, isohexyl, lauryl, octadecyl, isobornyl, 2-ethyloctyl, iso-octyl, n-octyl and 2-ethylhexyl acrylates and methacrylates. Some of these copolymers prepared in the fluorinated ether as reaction medium can be separated therefrom as stable polymer beads despite the absence of a stabilizer which is normally required to prepare such beads. For example, polymer beads of a copolymer of iso-octylacrylate and methacrylic acid can conveniently be prepared in this way. These polymers whether in the form of beads or not may be used to formulate a pressure sensitive adhesive.

The present invention therefore also provides a mixture of a fluorinated ether of the present invention and a copolymer of a fluorine free acrylate or methacrylate and acrylic or methacrylic acid. In particular, the present invention provides a mixture of a fluorinated ether and a copolymer of an alkyl acrylate or methacrylate of which the alkyl group has at least 4 carbon atoms and acrylic or methacrylic acid. The amount of solids of such a mixture will typically be in the range of 20% by weight to 60% by weight and more preferably between 30% by weight and 55% by weight.

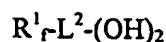
The fluorinated ethers can also be used as reaction medium for the polymerization of so called "fluoromonomers". By fluoromonomers are meant compounds that may be free radically polymerized, that contain at least one vinylic fluorine atom attached to the vinyl group that undergoes polymerization, and the compounds 3,3,3-trifluoropropene and 2-trifluoromethyl-3,3,3-trifluoro-1-propene. Examples of fluoromonomers containing a vinylic fluorine atom include vinyl fluoride; vinylidene fluoride; trifluoroethylene; chlorotrifluoroethylene (CTFE); 1,2-difluoroethylene; tetrafluoroethylene (TFE); hexafluoropropylene (HFP); perfluoro (alkyl vinyl) ethers such as perfluoro (methyl vinyl) ether (PMVE), perfluoro (ethyl vinyl) ether (PEMV), and perfluoro (propyl vinyl) ether (PPVE); perfluoro(1,3 dioxole); perfluoro(2,2-dimethyl-1,3-dioxole) (PDD);

- $\text{CF}_2=\text{CFOCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$; $\text{CF}_2=\text{CFOCF}_2\text{CF}_2\text{SO}_2\text{F}$;
 $\text{CF}_2=\text{CFOCF}_2\text{CF}_2\text{CF}_2\text{SO}_2\text{F}$; $\text{CF}_2=\text{CFOCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{CO}_2\text{F}$;
 $\text{CF}_2=\text{CFOCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{CH}_3$, $\text{F}(\text{CF}_2)_n\text{CH}_2\text{OCF}=\text{CF}_2$ where n is 1 to 5,
 $\text{R}_1\text{CH}_2\text{OCF}=\text{CF}_2$ where R_1 is hydrogen or $\text{F}(\text{CF}_2)_m$ and where m is 1, 2 or 3;
 5 $\text{R}_3\text{OCF}=\text{CH}_2$ where R_3 is $\text{F}(\text{CF}_2)_z$ and z is 1, 2, 3 or 4; perfluorobutyl ethylene
 (PFBE); 3,3,3-trifluoropropene; 2-trifluoromethyl-3,3,3-trifluoro-1-propene;
 $\text{CF}_2=\text{CFCl}$; and $\text{CF}_2=\text{CH}_2$.

The fluoromonomer may be polymerized alone to form a homopolymer if
 the fluoromonomer usually can be homopolymerized, or may be polymerized with
 10 one or more other fluoromonomers or other monomers which are not
 fluoromonomers to form a copolymer. If a copolymer is to be formed, the
 monomers chosen must be able to copolymerize. Such copolymerizable monomer
 combinations are known, see for example D. P. Carlson and W. Schmiegel, in
 W. Gerhartz, et al., Ed., Ullmann's Encyclopedia of Industrial Chemistry, 5th Ed ,
 15 vol. All, VCH Verlagsgesellschaft GmbH, Weinheim, 1988, p. 393-429, and various
 individual articles in H. Mark et al., Ed., Encyclopedia of Polymer Science and
 Engineering, John Wiley & Sons, New York, 1985, which descriptions are
 incorporated herein by reference. Comonomers that copolymerize with some
 combinations of fluoromonomers include propylene and ethylene.

20 The fluorinated ethers are also suitable for use as the reaction medium of
 polycondensation reactions which typically involve such flammable solvents as
 ethylacetate or methyl ethylketone. For example, the fluorinated ether can be used
 as the reaction medium for the polycondensation of a polyol, in particular a diol,
 and a compound having at least two acid groups, in particular carboxylic acid
 25 groups. Suitable polyols include alkane diols such as 1,4-butanediol, 1,3-
 propanediol and glycol, polyester diols and polyether diols. Suitable compounds
 containing two or more acid groups include dicarboxylic acids such as adipic acid,
 maleinic acid, succinic acid and barbituric acid. Typically, such polycondensation is
 carried out in the presence of a catalyst, in particular an acid catalyst such as p-
 30 toluenesulphonic acid. The fluorinated ethers are particularly suitable when the
 polycondensation involves a fluorochemical reactant. For example, in accordance

with a particular embodiment of the present invention, the polyol used is a fluorochemical polyol of the following formula (III):



wherein

- 5 R^1_f is a fluoroaliphatic radical, for example as described above for M_f ; and
 L^2 is an organic trivalent linking group, such as an alkylene, or an organic trivalent linking group corresponding to one of the following two formulas:



wherein L^3 , L^4 and L^5 each independently represent an organic divalent linking group such as a linear or branched alkylene or an arylene.

- 20 Examples of fluorochemical diols include those mentioned in U.S. Patent No. 4,046,944 (which description is incorporated herein by reference) and diols like $C_8F_{13}SO_2N(CH_2CH_2OH)_2$.

- The fluorinated ethers are further suitable for use as a reaction medium in a polycondensation of an epoxide and an alcohol to form a polyether. Suitable
 25 epoxides that can be used include epichlorohydrine, ethylene oxide and propylene oxide. Suitable alcohols include alkanols such as ethanol, propanol and butanol. Such reactions are preferably catalyzed using a catalyst such as $SnCl_4$. The fluorinated ethers are particularly preferred as the reaction medium of a polycondensation of a fluorochemical alcohol and an epoxide. Suitable
 30 fluorochemical alcohols include monofunctional fluoroaliphatic alcohols such as the N-alkanol perfluoroalkylsulfonamides described in U.S. Patent No. 2,803,656 (Ahlbrecht et al.) (which description is incorporated herein by reference). Illustrative of the fluoroaliphatic alcohols are the following: N-ethyl-N-(2-hydroxyethyl)-perfluorooctanesulfonamide, N-propyl-N-(2-hydroxyethyl)-

- perfluorooctanesulfonamide, N-ethyl-N-(2-hydroxyethyl)-
 perfluorodecanesulfonamide, N-ethyl-N-(2-hydroxyethyl)-
 perfluorododecanesulfonamide, N-ethyl-N-(2-hydroxyethyl)-
 perfluorocyclohexylethanesulfonamide, N-propyl-N-(2-hydroxyethyl)-
 5 perfluorobutylcyclohexanesulfonamide, N-ethyl-N-(2-hydroxyethyl)-perfluoro-4-
 dodecylcyclohexanesulfonamide, N-ethyl-N-(2-hydroxyethyl)-perfluoro-2-
 methylcyclohexanesulfonamide, N-ethyl-N-(6-hydroxyhexyl)-
 perfluorooctanesulfonamide, N-methyl-N-(11-hydroxyundecyl)-
 perfluorooctanesulfonamide, N-methyl-N-(4-hydroxybutyl)-
 10 perfluorobutanesulfonamide, N-(2-hydroxyethyl)-perfluorooctanesulfonamide and
 N-methyl-N-(2-hydroxyethyl)-perfluorooctanesulfonamide.

Still other alcohols include the perfluoroalkyl-substituted alkanols of the
 formula $C_nF_{2n+1}CH_2OH$, where n is 4 to 10 (e.g., $C_4F_9CH_2OH$), described, for
 example, in U.S. Patent No. 2,666,797 (Husted et al.) (which description is
 15 incorporated herein by reference), and of the formula $R_f(CH_2)_mOH$ where R_f is a
 perfluoroalkyl radical having from 4 to 10 carbon atoms and m is an-integer from 1
 to 4.

The fluorinated ether can further be used in a polycondensation reaction
 involving the use of a polyisocyanate. For example, the fluorinated ethers can be
 20 used as the reaction medium of a polycondensation of a polyisocyanate and a
 fluorochemical alcohol, including fluorochemical polyols and/or a hydrocarbon
 alcohol including hydrocarbon polyols. Examples of fluorochemical alcohols
 include those listed above. Examples of hydrocarbon alcohols include methanol,
 ethanol, ethylhexanol and the polyols exemplified above. Suitable polyisocyanates
 25 include aliphatic and aromatic isocyanates. Examples include aromatic
 diisocyanates such as 4,4'-methylenediphenylenediisocyanate, 4,6-di-
 (trifluoromethyl)-1,3-benzene diisocyanate, 2,4-toluenediisocyanate, 2,6-toluene
 diisocyanate, o, m, and p-xylylene diisocyanate, 4,4'-diisocyanatodiphenylether,
 3,3'-dichloro-4,4'-diisocyanatodiphenylmethane, 4,5'-diphenyldiisocyanate, 4,4'-
 30 diisocyanatodibenzyl, 3,3'-dimethoxy-4,4'-diisocyanatodiphenyl, 3,3'-dimethyl-4,4'-
 diisocyanatodiphenyl, 2,2'-dichloro-5,5'-dimethoxy-4,4'-diisocyanato diphenyl, 1,3-

diisocyanatobenzene, 1,2-naphthylene diisocyanate, 4-chloro-1,2-naphthylene diisocyanate, 1,3-naphthylene diisocyanate, and 1,8-dinitro-2,7-naphthylene diisocyanate; alicyclic diisocyanates such as 3-isocyanatomethyl-3,5,5-trimethylcyclohexylisocyanate; 3-isocyanatomethyl-3,5,5-trimethylcyclohexylisocyanate; aliphatic diisocyanates such as 1,6-hexamethylenediisocyanate, 2,2,4-trimethyl-1,6-hexamethylenediisocyanate, and 1,2-ethylenediisocyanate; aliphatic triisocyanates such as 1,3,6-hexamethylenetriisocyanate; aromatic tri-isocyanates such as polymethylenepolyphenylisocyanate (PAPI); cyclic diisocyanates such as isophorone diisocyanate (IPDI) and dicyclohexylmethane-4,4'-diisocyanate.

Also useful are isocyanates containing internal isocyanate-derived moieties such as biuret-containing tri-isocyanates such as that available from Bayer as DESMODUR™ N-100, isocyanurate-containing tri-isocyanates such as that available from Huls AG, Germany, as IPDI-1890, and azetidinedione-containing diisocyanates such as that available from Bayer as DESMODUR™ TT. Also, other di- or tri-isocyanates such as those available from Bayer as DESMODUR™ L and DESMODUR™ W, and tri-(4-isocyanatophenyl)-methane (available from Bayer as DESMODUR™ R) are suitable.

While the polyisocyanate might not be soluble in a reaction medium consisting of the fluorinated ether, it was found that urethanes and polyurethanes may nevertheless be prepared in this reaction medium and good yields can be obtained.

The fluorinated ethers are also suitable as a reaction medium in esterification reactions, in particular when one of the reactants, typically the alcohol is a fluorochemical reactant. For example, the fluorinated ethers can be used as the reaction medium in the preparation of an ester through the reaction of an alcohol and an acid chloride. Examples of alcohols that can be used are those listed above, including the fluorochemical alcohols listed above. Suitable acid chlorides include acryloyl and methacryloyl chloride which allow for the preparation of a fluorochemical monomer as described above, acetic acid chloride, phthaloylic acid chloride and benzoic acid chloride. These reactions are typically carried out in the

presence of a basic catalyst capable of scavenging the hydrochloric acid formed during the reaction. A typical catalyst is triethylamine.

Alternatively, esters can be prepared by reacting an acid with an alcohol preferably in the presence of a catalyst such as p-toluenesulphonic acid. Also in this
5 type of esterification, the fluorinated ether has been found to be a suitable reaction medium. For example, the fluorinated ether can be used as the reaction medium in the reaction of (meth)acrylic acid or adipic acid and an alcohol such as n-octanol, n-dodecanol, ethylene glycol, isopropanol or $\text{CH}_2=\text{CH}-\text{CH}_2\text{OH}$.

Transesterifications wherein an ester is reacted with an alcohol typically in
10 the presence of a catalyst, for example an acid catalyst, may also be carried out in the fluorinated ether as reaction medium. In this instance, it is preferred that the fluorinated ether used as reaction medium is immiscible, at least at ambient temperature, with the alcohol formed during the reaction. This facilitates the separation of the reaction product.

15 The fluorinated ethers are further a suitable reaction medium for the preparation of an enamine from a ketone and an amine. For example the fluorinated ether can be used to react morpholine with cyclohexanone to prepare the corresponding enamine. Such reaction is preferably carried out with the aid of a catalyst such as p-toluenesulphonic acid.

20 The suitability of the fluorinated ethers as a reaction medium for various organic reactions is illustrated by the following examples without the intention to limit the invention thereto. All parts are by weight unless otherwise indicated.

EXAMPLES

25 In the examples, the following test methods and abbreviations are used:

Test methods

GLC analysis

30 GLC-analysis was done with a Hewlett Packard 5890 gas chromatograph using a Econocap SE 54 column having a length of 30m, a diameter of 250 μm and a film thickness of 0.25 μm .

Determination of weight average molecular weight (Mw)

Molecular weights of the polymers were determined by means of a Waters GPC equipped with a refractive index detector. Hexafluoroisopropanol was used as
5 a solvent and polymethylmethacrylate was used as a reference standard.

Contact angle measurement

A 2% solution of polymer in fluorinated ether was prepared. A glass plate of 3 cm x 10 cm was dipped into the solution and dried at room temperature. The
10 contact angle for different solvents was measured using an Olympus TGHM goniometer.

Inherent viscosity (IV)

The inherent viscosity of the polymers was measured by conventional means
15 using a Cannon-Fenske 50 viscosimeter in a water bath controlled at 25°C to measure the flow time of 10 ml of a polymer solution (0.15 g of polymer in 100 ml methylethyl ketone). Inherent viscosity is recorded as dl/g.

List of abbreviations

- 20 DI-water : deionised water
V-65 : 2,2'-azobis(2,4-dimethyl valeronitrile), available from Wako
MEHQ : methylhydroquinone
MeFOSEMA : $C_8F_{17}SO_2N(CH_3)CH_2CH_2OC(O)C(CH_3)=CH_2$
BuFOSE : $C_8F_{17}SO_2N(Butyl)CH_2CH_2OH$
25 BuFOSEA : $C_8F_{17}SO_2N(Butyl)CH_2CH_2OC(O)CH=CH_2$
PAPI : polymethylenepolyphenylisocyanate, available from Dow Chemical
IBMA : isobutylmethacrylate
ODMA : octadecyl methacrylate
AMA : allyl methacrylate
30 MA : Maleic anhydride
AAEMA : 2-hydroxyethyl methacrylate ester of acetoacetic acid, available from

Lonza

DCPOEMA : dicyclopentenyl oxy ethyl methacrylate, available from Wako

AIBN : 2,2'-azo bisisobutyronitrile

MEK : methylethylketone

5 THF : tetrahydrofuran

EtOAc : ethylacetate

IOTG : isooctyl thioglycolate, available from Elf Atochem

IOA : isooctyl acrylate

AA : acrylic acid

10 MAA : methacrylic acid

DMAcAm : dimethyl acrylamide

Uvecryl™ P-36 : benzophenone derivative of acrylic acid, available from UCB

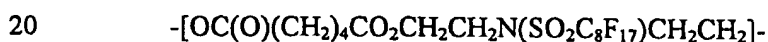
BMA : butyl methacrylate

LMA : lauryl methacrylate

15 CHPMA : (3-chloro-2-hydroxypropyl)-methacrylate

VCL₂ : vinylidenechloride

Example 1



A 250 mL flask was equipped with a magnetic stirrer, thermometer, a modified Dean-Stark trap and nitrogen inlet. The flask was charged with adipic acid (2.92 g, 20 mmole), n-C₈F₁₇SO₂N(CH₂CH₂OH)₂ (11.74g, 20 mmole), perfluorononyl methyl ether (C₉F₁₉OCH₃, 100 g) and p-toluenesulfonic acid (0.2 g).

25 The reaction mixture was heated to reflux for 24 hours under nitrogen and water was collected in the Dean-Stark trap. The perfluorononyl methyl ether was distilled from the reaction mixture yielding a solid polymer product. Analysis of the product by gel permeation chromatography revealed Mw/Mn = 6486/5036 corresponding to a degree of polymerization of about 9.

30

Example 2

Using essentially the procedure of Example 1, the flask was charged with adipic acid (2.92 g, 20 mmole), n-C₈F₁₇SO₂N(CH₂CH₂OH)₂ (11.74g, 20 mmole), perfluoroheptyl methyl ether (C₇F₁₅OCH₃, 100 g) and titanium isopropoxide
 5 (0.5 g). The reaction mixture was heated to reflux for 24 hours under nitrogen and water was collected in the Dean-Stark trap. The perfluoroheptyl methyl ether was distilled from the reaction mixture yielding a sticky product. Analysis of the product by gel permeation chromatography revealed Mw/Mn = 3613/3399 corresponding to a degree of polymerization of about 5.

10

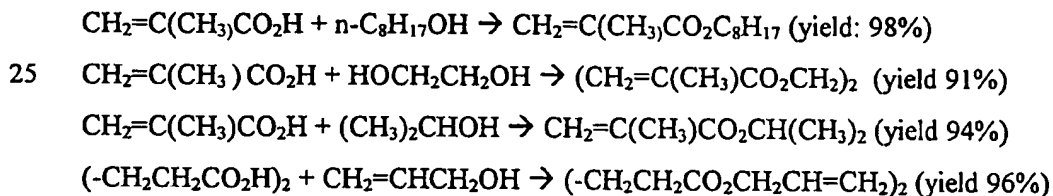
Example 3

Preparation of allyl methacrylate

Using essentially the procedure of Example 1, the flask was charged with methacrylic acid (8.6 g, 0.1 mole), allyl alcohol (5.8 g, 0.1 mole), p-toluenesulfonic
 15 acid monohydrate (0.6 g) and perfluorobutyl methyl ether (70 g). The mixture was heated to reflux for four hours, filtered, and distilled to recover the perfluorobutyl methyl ether. The residue was then distilled under vacuum to yield allyl methacrylate (10 g, b.p. 70-1°C at 5 torr, purity 93% by GC).

20 Examples 4 to 7

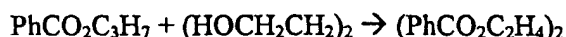
To demonstrate the versatility of fluorinated ethers as reaction media in esterifications the following reactions were also run using essentially the procedure of Example 1 and the yields obtained are indicated:

Example 8

30 Using essentially the procedure of Example 1, the flask was charged with morpholine (8.7 g, 0.1 mole) and hexanone (10.1 g, 0.1 mole) in perfluorobutyl

ethyl ether (60 g). After refluxing for ten hours, the fluorinated ether was removed by flash distillation and water (20 mL) was added to the residue. The resultant mixture was extracted with diethyl ether, the combined ether extracts washed with water, dried over magnesium sulfate and distilled to yield the desired enamine (10.6 g, b.p. 73-4°C at 0.35 torr).

Example 9



Using essentially the procedure of Example 1, the flask was charged with PhCO₂C₃H₇ (34 g, 0.2 mole), 1,4-butane diol (9.1 g, 0.1 mole) and p-toluenesulfonic acid monohydrate (0.5 g) and perfluoroheptyl methyl ether (160 g). The reaction was heated to reflux for ten hours. The upper layer collected in the Dean-Stark trap was collected and identified as n-propanol, which was insoluble in the fluorinated ether at room temperature. The contents of the reaction flask was collected and the upper products layer separated and solidified on cooling (29.1 g, 97% yield). The product was further purified by recrystallization from methylene chloride/hexane (m.p. 82-3°C).

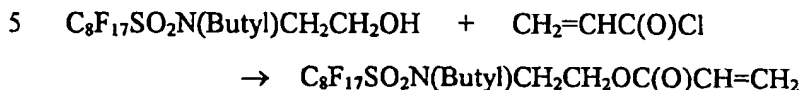
Example 10



A 500 ml three necked reaction flask, equipped with a stirrer, a thermometer, a condenser and a heating mantle was charged with 80 g (0.2 moles) C₇F₁₅CH₂OH, 80 g perfluorobutyl methyl ether and 22.2 g triethylamine (0.22 moles). The mixture was cooled to 5°C in an ice bath under nitrogen atmosphere. 22.9 g methacryloylchloride (0.22 moles) were added over a period of 30 minutes while maintaining the temperature between 5 and 10°C. After the addition was complete, the reaction was kept at room temperature for one hour. After addition of 0.1 g MEHQ, the reaction was heated to 50°C for 1 hour. The reaction mixture was analyzed by GLC, showing a conversion to fluorochemical methacrylate of about 97%. The reaction mixture was washed 3 times at room temperature, using 200 ml water and then with 200 ml of a 5% sodium carbonate solution. A clear solution of

50% fluorochemical monomer $C_7F_{15}CH_2OC(O)C(CH_3)=CH_2$ in perfluorobutyl methyl ether was obtained.

Example 11



Using essentially the procedure described in example 10, BuFOSE was converted to BuFOSEA using acryloylchloride. A conversion of 95% was obtained as measured with GLC.

10

Examples 12 to 15 and comparative examples C-1 to C-3

Examples 12 to 15 illustrate the versatility of hydrofluoro ethers as reaction medium for the copolymerization of fluorochemical acrylate monomers with fluorine free monomers.

15

Example 12: A three necked flask equipped with a stirrer, heating mantle, thermometer and condenser was charged with 14.7 g (0.036 moles) $C_7F_{15}CH_2OC(O)C(CH_3)=CH_2$, 0.3 g (0.004 moles) acrylic acid, 85 g perfluorobutyl methyl ether and 0.2 g V-65 initiator under nitrogen atmosphere. The polymerization reaction was run at 70°C for 16 hours after which another 0.1 g V-65 was added and the reaction was continued for 3 hours. A clear, slightly yellow solution was obtained. GLC indicated that the conversion was about 96%.

20

Examples 13 to 15 were made following the same procedure as for Example 12, using the monomers as given below.

25

Example 13 : $C_7F_{15}CF(CF_3)COOCH_2CH_2OC(O)CH=CH_2$ (14.7 g) + AA (0.3 g)

Example 14 : $C_7F_{15}CH_2OC(O)C(CH_3)=CH_2$ (14.7g) + AA (0.3g) + Uvecryl™ P-36 (0.1g)

Example 15 : MeFOSEMA (8.55 g) + BMA (3.3 g) + LMA (3.0 g) + MAA (0.15 g)

30

In Comparative Example C-1, the polymerization procedure of Example 12 was repeated, but the perfluorobutyl methyl ether was replaced by $\text{HCF}_2\text{CF}_2\text{CH}_2\text{OCH}_3$ as the reaction medium. GLC analysis indicated a conversion of 92%. In comparative examples C-2 and C-3, the fluorinated ether was replaced by butylacetate and a perfluorocarbon, respectively. The polymers prepared in Examples 12 to 15 were evaluated for their contact angle and their molecular weight and compared to polymers of Examples C-1 to C-3. The results are given in Table 1.

10

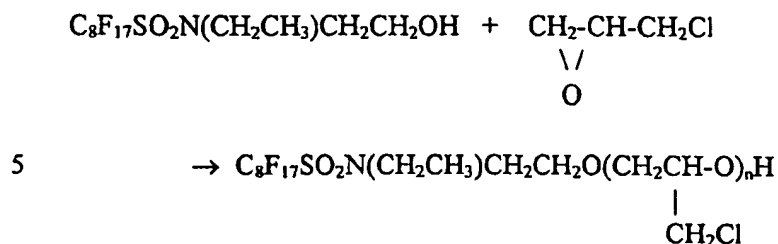
Table 1 : Characteristics of Fluorochemical Polymers

Ex No	Contact angle DI-water	Contact angle Hexadecane	Weight average Mw
12	120°	67°	22200
13	118°	70°	22300
14	118°	65°	22100
15	115°	60°	22100
C-1	102°	53°	10600
C-2	110°	56°	14700
C-3	119°	62°	25000

The results indicate that the fluorinated ethers are suitable as reaction medium for the polymerization of a fluorochemical monomer and a non-fluorochemical monomer. Similar contact angles and molecular weight was obtained for polymers prepared in the fluorinated ether of the invention as compared to a polymer prepared in a perfluorocarbon solvent or butylacetate. Compared to the ether of Example C-1, much higher molecular weight polymers were obtained.

20 Example 16

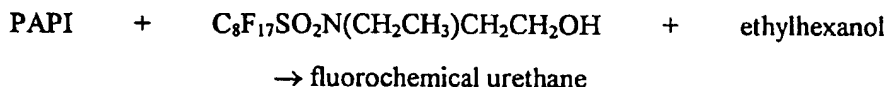
Example 16 illustrates the use of the fluorinated ether as reaction medium for a ring opening reaction.



A dry, three necked flask, equipped with a stirrer, condenser, heating mantle and thermometer was charged with 58.0 g (0.1 mole) $C_8F_{17}SO_2N(CH_2CH_3)CH_2CH_2OH$, 60 g perfluorobutyl methyl ether and 11.0 g (0.12 moles) epichlorohydrine. The reaction mixture was heated to 50°C and covered with nitrogen atmosphere. Then 0.2 g $SnCl_4$ was added dropwise over 30 minutes, then the reaction was heated to reflux (60°C) under nitrogen during 16 hours. A clear, slightly amber solution was obtained. GLC-analysis indicated that adducts with a general formula as given above were formed with : $n=0$: 22% ; $n=1$:45% ; $n=2$:20% ; $n=3$:8% and $n=4$:<1%.

Example 17

20 This example demonstrates the use of the fluorinated ethers as reaction medium in condensation reactions. A fluorochemical urethane was made starting from the following reactants:



25 In a three necked flask of 250 ml, equipped with a stirrer, heating mantle, thermometer and condenser were placed 20.2 g (about 0.15 NCO equivalents) polymeric isocyanate PAPI, 58 g (0.1 moles) $C_8F_{17}SO_2N(CH_2CH_3)CH_2CH_2OH$, 6.5 g (0.05 moles) ethylhexanol and 90 g perfluorobutyl methyl ether. The reaction mixture was heated to 50°C under nitrogen atmosphere. Then 0.1 g stannous octoate catalyst was added and the reaction was heated to reflux (60°C) for 40 hours. A hazy solution was obtained. IR analysis indicated that all isocyanate had reacted and that urethane formation had taken place. This example showed that, although the isocyanate was not soluble in the fluorinated ether, fluorochemical urethane could be made by using the fluorinated ether as reaction medium.

Examples 18 to 25

In Examples 18 to 25 fluorochemical acrylates were homopolymerized or copolymerized with fluorine-free monomers, using perfluorobutyl methyl ether as
5 reaction medium. The polymers were made at 30% solids using 0.3% AIBN as initiator. The reactions were run at 70°C, for 16 hours. The monomer compositions are given in Table 2.

Table 2 : Composition of Fluorochemical Polymers
Made in Perfluorobutyl Methyl Ether

	Ex 18	Ex 19	Ex 20	Ex 21	Ex 22	Ex 23	Ex 24	Ex 25
MeFOSEMA	100	90	70	90	80	80	80	80
LMA	-	10	30	-	-	-	-	-
ODMA	-	-	-	10	20	10	-	13
AAEMA	-	-	-	-	-	10	-	-
Styrene	-	-	-	-	-	-	20	7
MA	-	-	-	-	-	-	2	-
Appearance after reaction	viscous hazy solution	slightly viscous hazy solution	viscous hazy solution	viscous hazy solution	emulsion	viscous clear liquid	viscous clear solution	viscous clear solution

It has been observed that fluorochemical copolymers could be made in the fluorinated ether, even if one of the monomers, e.g., ODMA was not soluble in the reaction medium.

The experiments indicated that when more fluorine-free monomer was used, the viscosity of the polymer solution increased (e.g., Example 20 more viscous than Example 19). It also showed that when fluorine-free monomers with longer alkyl chains were used, the viscosity increased (e.g., Example 21 more viscous than Example 19) and that longer chain alkyl groups could lead to the formation of emulsions (e.g., Example 22) when used in higher amounts.

10

Examples 26 to 36

In Examples 26 to 36 essentially the same procedure as for Examples 18 to 25 was used to prepare copolymers of fluorochemical acrylates with various non-fluorochemical monomers described in Table 3. The polymers were made at 30% solids, using 1.2 parts lauroylperoxide as initiator and 0.3 parts n-octylmercaptane as chain transfer agent. The reactions were run at 70°C for 20 hours.

15

Table 3 Composition of Fluorochemical Polymers

Ex No	MeFOSEMA	ODMA	AMA	MA	Other
26	24	6	0.6	0.3	--
27	24	6	1.2	0.3	--
28	24	6	1.2	1.2	--
29	24	6	1.2	--	--
30	24	6	0.9	0.9	--
31	24	--	0.9	0.9	6 LMA
32	24	--	0.9	0.9	6 IBMA
33	24	4.5	0.6	0.6	1.5 AAEMA
34	24	3	--	--	3 AAEMA
35	24	3	--	--	3 CHPMA
36	24	6	--	--	1.2 DCPOEMA

After polymerization, all polymer solutions were viscous clear solutions, except for Example 29 which was a hazy viscous solution.

Examples 37 to 40

5 In Examples 37 to 40 fluorochemical polymers were made using vinylidene chloride as comonomer. The reactions were carried out at 30% solids in a mixture of perfluorobutyl methyl ether (66.5 parts) and n-butylglycidylether (3.5 parts ; added to stabilize the vinylidene chloride containing polymer formed). 1.2 parts lauroyl peroxide was used as initiator and 0.3 parts n-octyl mercaptane were added
10 as chain transfer agent. The reactions were run at 70°C during 20 hours. The composition and appearance after reaction are given in Table 4.

Table 4: Composition of Vinylidene Chloride Containing Polymers

Ex No	MEFOSEMA	ODMA	VCl ₂	AAEMA	Appearance after reaction
37	24	--	6	--	milky emulsion
38	24	3	3.9	--	emulsion
39	24	4.5	1.5	--	slightly hazy solution
40	24	3	1.5	1.5	yellow clear solution

Examples 41 and 42

15 Examples 41 and 42 illustrate the use of the fluorinated ethers as reaction medium to make non-fluorochemical polymers. In these examples respectively IOA/AA 90/10 and IOA/MAA 90/10 monomer mixtures were polymerized under nitrogen atmosphere in perfluorobutyl methyl ether, at 40% solids, using 0.2% V-65
20 as initiator. The reaction was carried out for 24 hours at 45°C. While the monomer mixtures were soluble in the reaction medium, during the reaction the polymers formed precipitated and could be easily separated from the solvent. After polymerization, the polymers were isolated and dried in an oven. The polymers formed were not soluble in common used solvents, such as ethylacetate, THF or
25 MEK, indicating high molecular weight polymer was made.

Examples 43 to 45

Examples 43 to 45 were carried out following essentially the same procedure used in examples 41 and 42, but with lower amount of solids. The polymers were made at 45°C at 30% solids, using 0.2% V-65. Comparative

- 5 Examples C-4 to C-6 were made in ethylacetate as solvent. The results are given in Table 5.

Table 5: Composition of Non-Fluorinated Polymers

Ex No	IOA	AA	MAA	DMAcAM	Result after polymerization
43	90	10	--	--	precipitate
44	90	--	10	--	precipitate
45	80	--	--	20	precipitate
C-4	90	10	--	--	IV 1.21
C-5	90	--	10	--	nonhomogeneous mixture
C-6	80	--	--	20	IV 1.29

- 10 The polymers made in the fluorinated ether precipitated during the reaction and could be easily separated from the reaction mixture. Again they were not soluble in common solvents, indicating high molecular weight material was obtained. Comparative Examples C-4 and C-6 formed viscous polymer solutions, which were soluble in MEK and for which IV could be measured. In Comparative
- 15 Example C-5, a very nonhomogeneous mixture with high viscous solution and some solid polymer was formed. This shows that for certain monomer compositions such as IOA/MAA, with MAA used at rather high concentrations, it was not possible to make a copolymer in ethylacetate, whereas the mixture can be polymerized in the fluorinated ether.

20

Examples 46 to 48 and Comparative Examples C-7 to C-9

Examples 46 to 48 were carried out essentially according to the procedure of Examples 43 to 45. In order to further lower the molecular weight, a chain transfer agent was added. The polymers were made at 30% solids using 0.2% V-65

and 0.5% IOTG. The reaction was run at 45°C for 24 hours. Comparative Examples C-7 to C-9 were made in the same way, but using ethylacetate as solvent. The composition of the polymers and the results are given in Table 6.

5 Table 6 : Composition and Results of Non-Fluorochemical Polymers

Ex No	IOA	AA	MAA	DMAcAM	IV (MEK)
46	90	10	--	--	0.14
47	90	--	10	--	0.15
48	80	--	--	20	0.54
C-7	90	10	--	--	0.13
C-8	90	--	10	--	nonhomogeneous mixture
C-9	80	--	--	20	0.19

Again, no polymer could be made from the IOA/MAA 90/10 mixture in ethylacetate.

10 Another observation was that the polymers, made in fluorinated ether precipitated as polymer beads, which could easily be handled. Surprisingly these polymer beads were stable despite the absence of a stabilizing agent, normally used to stabilize polymer beads prepared in suspension polymerization.

We Claim:

1. Method for preparing a desired organic compound by reacting one or more reactants in a reaction medium, said reaction medium comprising a fluorinated ether and said fluorinated ether comprising at least 3 carbon atoms and a perfluorinated moiety linked through ether oxygen atoms to one or more hydrocarbon moieties.
2. A method according to claim 1 wherein said reaction medium in non-flammable.
3. A method according to claim 1 wherein said fluorinated ether is non-flammable.
4. A method according to claim 1 wherein the desired organic compound is prepared by reacting one or more reactants via a reaction selected from the group consisting of free radical polymerization reactions, polycondensation reactions, oxidation and reduction reactions, radical addition reactions, nucleophilic addition reactions, electrophilic addition reactions and nucleophilic and electrophilic substitution reactions.
5. A method according to claim 1 wherein said desired organic compound is a fluorochemical compound and wherein one or more of said reactants comprise a fluorochemical group.
6. A method according to claim 1 wherein said desired organic compound is a polymer and said reactants comprise at least one monomer and wherein said method comprises polymerization of said at least one monomer to form said polymer.

7. A method according to claim 6 wherein said reactants further comprise a free radical initiator and said polymerization is a free radical polymerization.

5 8. A method according to claim 6 wherein said polymerization is a polycondensation.

9. A method according to claim 6 wherein said reactants comprise at least one fluorinated monomer.

10

10. A method according to claim 9 wherein said fluorinated monomer corresponds to the following formula:



wherein

15 M_f represents a partially fluorinated or perfluorinated aliphatic group,
 L^1 represents an organic divalent linking group and
E represents an ethylenically unsaturated group.

11. A method according to claim 10 wherein said polymerization is a
20 copolymerization of said fluorinated monomer and at least one non-fluorinated monomer.

12. A method according to claim 7 wherein said polymerization is a
copolymerization of an alkyl acrylate having an alkyl group of at least 4 carbon
25 atoms and/or an alkyl methacrylate having an alkyl group of at least 4 carbon atoms
and acrylic acid or methacrylic acid.

13. A method according to claim 1 wherein at least one of said reactants
is dissolved in said reaction medium.

30

14. A method according to claim 1 wherein at least 50% by weight of said reaction medium consists of said fluorinated ether.
15. A method according to claim 1 wherein said method comprises a reaction selected from the group consisting of an esterification and a transesterification.
16. A method according to claim 1 wherein one or more of said reactants comprises an isocyanate group and one or more other reactants comprise a group capable of reaction with an isocyanate.
17. A method according to any of claims 1 to 16, wherein :
- (a) said perfluorinated moiety is a perfluoroaliphatic moiety comprising at least two carbon atoms, and
- (b) said one or more hydrocarbon moieties are alkyl moieties comprising one to four carbon atoms.
18. A method according to claim 17, wherein the fluorinated ether corresponds to the following formula:
- $$(R_h-O)_x-R_f \quad (I)$$
- wherein:
- x is 1 or 2;
- R_h represents an alkyl group having 1 to 4 carbon atoms;
- R_f represents a perfluorinated aliphatic group comprising about two to ten carbon atoms.
19. A method according to claim 18 wherein x is 1 and R_f is selected from the group consisting of linear or branched perfluoroalkyl groups, perfluorocycloalkyl groups containing a perfluoroalkyl group, perfluorocycloalkyl groups, linear or branched perfluoroalkyl groups having one or more catenary heteroatoms, perfluorocycloalkyl groups containing a perfluoroalkyl group and

having one or more catenary heteroatoms and perfluorocycloalkyl groups having one or more catenary heteroatoms.

20. A method according to claim 18 wherein, x is 2 and R_f is selected
5 from the group consisting of linear or branched perfluoroalkylene groups, perfluorocycloalkyl groups containing a perfluoroalkylene group, perfluorocycloalkylene groups, linear or branched perfluoroalkylene groups having one or more catenary heteroatoms, perfluorocycloalkyl groups containing a perfluoroalkylene group having one or more catenary heteroatoms and
10 perfluorocycloalkylene groups having one or more catenary heteroatoms.

21. A method according to claim 18 wherein the compound is normally liquid or gaseous, x is 1 and R_f is selected from the group consisting of linear or branched perfluoroalkyl groups having from 3 to about 9 carbon atoms,
15 perfluorocycloalkyl-containing perfluoroalkyl groups having from 5 to about 7 carbon atoms, and perfluorocycloalkyl groups having from 5 to about 6 carbon atoms; and R_h is a methyl or ethyl group and the sum or the number of carbon atoms in R_f and R_h is about 4.

20 22. A fluorochemical composition comprising:
(a) a copolymer of a fluorochemical monomer that comprises a fluorinated group and an ethylenically unsaturated group free of fluorine and a non-fluorinated monomer; and
(b) a fluorinated ether comprising at least 3 carbon atoms and a
25 perfluorinated moiety linked through ether oxygen atoms to one or more hydrocarbon moieties.

23. A fluorochemical composition according to claim 22 wherein said copolymer is a copolymer of a fluorinated monomer comprising a fluorinated group
30 and an α,β ethylenically unsaturated carbonyl group and a non-fluorinated

monomer that comprises an α,β ethylenically unsaturated carbonyl group and wherein said copolymer is dissolved in said fluorinated ether.

24. A fluorochemical composition according to claim 23 comprising said
5 copolymer in an amount of 0.01% by weight and 50% by weight.

25. A method for applying a protective coating comprising the step of applying a coating as defined in any of claims 22 to 24 to a substrate.

10 26. A method for applying a protective coating comprising the step of applying a coating as defined in any of claims 22 to 24 to an electronic component.

27. A mixture comprising (a) a fluorine free copolymer of acrylic or methacrylic acid and an alkyl acrylate having at least 4 carbon atoms in the alkyl
15 group or an alkyl methacrylate having at least 4 carbon atoms in the alkyl group; and (b) a fluorinated ether comprising at least 3 carbon atoms and a perfluorinated moiety linked through ether oxygen atoms to one or more hydrocarbon moieties.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 97/17458

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08G63/688 C07C67/08 C07C67/03 C07C303/40 C08F220/24
C08F220/38 C08F2/06 C08F220/06 C08G18/38 C08J7/04
C08J3/09 //C07C69/54, C07C69/44, C07D295/02, C07C69/48,

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08G C07C C07D C08F C08J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 97 28229 A (E.I. DU PONT DE NEMOURS AND CO) 7 August 1997 see page 3, line 29 - page 4, line 30, in particular page 4, line 7; page 6, line 34 - page 7, line 22	1, 3, 14, 17-19, 21
Y	see idem	1, 3-7, 9, 13, 14, 17-19, 21
Y	US 5 182 342 A (A.E. FEIRING ET AL) 26 January 1993 cited in the application see column 3, lines 12 -42; claims	1, 3-7, 9, 13, 14, 17-19, 21
A	US 4 043 965 A (R.E. DICKSON) 23 August 1977 see example 1	1, 6, 7, 9-12

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B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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INTERNATIONAL SEARCH REPORT

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